APPLICATION

FOR

UNITED STATES LETTERS PATENT

TITLE: **THERMAL EXTENDERS FOR WELL FLUID APPLICATIONS**

APPLICANT: **David P. KIPPIE**
William E. FOXENBERG
Robert L. HORTON

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Thermal Extenders for Well Fluid Applications

Cross-Reference to Related Applications

[0001]   This Application claims the benefit of U.S. Provisional Patent Application No. 60/295,381, filed on June 1, 2001.

Background of Invention

Field of the Invention

[0002]   The invention relates generally to the exploitation of hydrocarbon-containing formations. More specifically, the invention relates to the fields of fluid rheology, thickeners, viscosifiers, viscoelastic fluids, drilling fluids, well fracturing fluids, well treatment fluids and fluid control pills. The present invention teaches compositions for the creation of and methods of using fluid loss control pills and similar fluids that can sustain stress conditions for extended periods of time without significant fluid loss or loss of desirable rheological properties. The stress conditions may include, for example, exposure to high shear in pumping and placement, exposure to oxidative breakers, high temperature, high differential pressure, low pH, extended time, and a combination of two or more of said stress conditions. These pills and fluids are advantageously applied in or in connection with drilling, drill-in, displacement, completion, hydraulic fracturing, work-over, packer fluid implacement or maintenance, well treating, testing, or abandonment.

Background Art

[0003]   When drilling or completing wells in earth formations, various fluids typically are used in the well for a variety of reasons. The fluid often is aqueous.

For the purposes herein, such fluid will be referred to as "well fluid." Common uses for well fluids include: lubrication and cooling of drill bit cutting surfaces while drilling generally or drilling-in (*i.e.*, drilling in a targeted petroliferous formation), transportation of "cuttings" (pieces of formation dislodged by the cutting action of the teeth on a drill bit) to the surface, controlling formation pressure to prevent blowouts, maintaining well stability, suspending solids in the well, minimizing fluid loss into and stabilizing the formation through which the well is being drilled, fracturing the formation in the vicinity of the well, displacing the fluid within the well with another fluid, cleaning the well, testing the well, implacing a packer fluid, abandoning the well or preparing the well for abandonment, and otherwise treating the well or the formation. Brines (such as $CaBr_2$) commonly are used as well fluids because of their wide density range and the fact that brines are typically substantially free of suspended solids. Additionally, brines typically do not damage certain types of downhole formations.

[0004]   A variety of compounds typically are added to the brine-based well fluids. For example, a brine-based well fluid also may include corrosion inhibitors, lubricants, pH control additives, surfactants, solvents, and/or weighting agents, among other additives. Some typical brine-based well fluid viscosifying additives include xanthan gum and hydroxyethyl cellulose (HEC).

[0005]   The natural and natural derivative polymers and oligomers listed above have other uses in drilling applications as well. When drilling progresses to the level of penetrating a hydrocarbon bearing formation, special care may be required to maintain the stability of the wellbore. Examples of formations in which problems often arise are highly permeable and/or poorly consolidated formations. In these types of formations, a technique known as "under-reaming" may be employed.

[0006]   In this process, the wellbore is drilled to penetrate the hydrocarbon bearing zone using conventional techniques. A casing generally is set in the wellbore to a point just above the hydrocarbon bearing zone. The hydrocarbon zone then may be re-drilled, for example, using an expandable under-reamer that increases the diameter of the wellbore. Under-reaming usually is performed using special "clean" drilling fluids. Typical drilling fluids used in under-reaming are expensive, aqueous, dense brines that are viscosified with a gelling and/or cross-linked polymer to aid in the removal of formation cuttings. The high permeability of the target formation, however, may allow large quantities of the drilling fluid to be lost into the formation.

[0007]   Once the drilling fluid is lost into the formation, it becomes difficult to remove. Calcium and zinc-bromide brines can form highly stable, acid insoluble compounds when reacted with the formation or substances contained therein. This reaction may reduce the permeability of the formation to any subsequent out-flow of the targeted hydrocarbons. The most effective way to prevent such damage to the formation is to limit fluid loss into the formation.

[0008]   Thus, providing effective fluid loss control is highly desirable to prevent damaging the formation in, for example, completion, drilling, drill-in, displacement, hydraulic fracturing, work-over, packer fluid implacement or maintenance, well treating, or testing operations. Techniques that have been developed to control fluid loss include the use of fluid loss "pills." Significant research has been directed to determining suitable materials for the fluid loss pills, as well as controlling and improving the properties of the fluid loss pills. Typically, fluid loss pills work by enhancing filter-cake buildup on the face of the formation to inhibit fluid flow into the formation from the well bore.

[0009]   Because of the high temperature, high shear (caused by the pumping and placement), high pressures, and low pH to which well fluids are exposed ("stress

conditions"), the polymeric materials used to form fluid loss pills and to viscosify the well fluids tend to degrade rather quickly. In particular, for many of the cellulose and cellulose derivatives (such as HEC) used as viscosifiers and fluid control loss agents, significant degradation occurs at temperatures around 200 °F and higher. HEC, for example, is considered sufficiently stable to be used in an environment of no more than about 225 °F. Likewise, because of the high temperature, high shear, high pressures, and low pH to which well fluids are exposed, xanthan gum is considered sufficiently stable to be used in an environment of no more than about 290 to 300°F, or about 320 to 330°F in the presence of salts of formate / acetate anions.

[0010]   What is needed are natural and natural derivative polymer compositions that can withstand the stress conditions for extended periods of time without significant degradation. In particular, what is needed is a simple, inexpensive way to increase the thermal range for viscosifying agents used in downhole applications. Preferably, this thermal extender would be applicable to various viscosifying agents (unlike the salts of formate or acetate anions, which only work for xanthan gum).

Summary of Invention

[0011]   In one aspect, the present invention relates to a method for increasing the thermal stability of viscosifying agents, and particularly polymers, used in a well fluid which comprises mixing a miscible tertiary amine compound into the fluid.

[0012]   In another aspect, the present invention relates to a method for increasing the thermal stability of viscosifying agents, and particularly polymers, in a well fluid which comprises mixing a miscible secondary amine compound into the fluid.
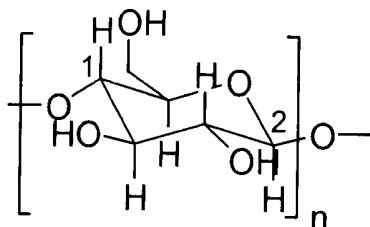
[0013]   In another aspect, the present invention relates to a thermally stable viscosifying system for well fluids which comprises a polymer, a solvent, and a tertiary amine miscible in the solvent.

[0014]   In another aspect, the present invention relates to a thermally stable viscosifying system for well fluids, which comprises a polymer, a solvent, and a secondary amine miscible in the solvent.

[0015]   Other aspects and advantages of the invention will be apparent from the following description and the appended claims.
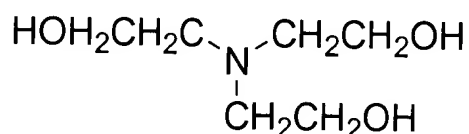
Detailed Description

[0016]   The present invention discloses a novel composition for increasing the thermal durability of natural and natural derivative polymers used in downhole applications. In general, the invention, in one embodiment, involves the effect of triethanol amine (TEA) on a conventional liquid viscosifier, such as hydroxyethyl cellulose (HEC). HEC is a derivative of cellulose, where the pendant hydroxyl moieties have been replaced with hydroxyethyl ether groups. The presence of these long side chains prevent the individual polymer strands from aligning and crystallizing, which allows HEC to be water soluble. The general structure of a cellulose polymer is shown below.

Eq. 1

[0017]   Triethanol amine (TEA) has the following structure:

$$HOH_2CH_2C \underset{\underset{CH_2CH_2OH}{|}}{N} CH_2CH_2OH$$

Eq. 2

[0018]   In a first embodiment, the effects of high temperatures for long periods of time were measured on a TEA-containing composition. Specifically, 13.3 milliliters (mL) of TEA was added to a brine / HEC mixture. The brine / HEC mixture was formed by the addition of 12.0 mL of an HEC suspension (41% by weight active component of HEC in dipropylene glycol methyl ether) to the brine solution. In this embodiment, the brine solution consisted of 0.965 lab barrels (Lbbl) of a 13.8 pounds per gallon (ppg) $CaBr_2$ in water. All of the use of the word "barrel" in this specification relates to "lab barrels" - a lab barrel is equivalent to about 350 milliliters. (A lab barrel of water weighs about 350 grams, just as a regular barrel of water weighs the same number of pounds, about 350. This is the formal origin of the term "lab barrel." Fortunately, a lab barrel of any fluid – regardless of density – happens to have the same volume as that of a lab barrel of water). Additionally, while the particular embodiments describe a particular order of addition for the chemical components, such a description is not intended to limit the scope of the invention in any fashion.

[0019]   After mixing the components, initial rheological parameters were measured. The rheological measurements were made using a Fann model 35 rotational viscometer (manufactured by Fann Instrument Co., of Houston, Texas), using a B1 bob on a "2 times" spring. Specifically, the apparent viscosity was measured. Viscosity is the ratio of the shear stress to the shear rate and is an indication of flow resistance. For many fluids, apparent viscosity changes for different values of shear rate, and is measured in centiPoise (cP). Shear rate is measured in RPM or sec^{-1}.

[0020]   In this embodiment, the initial apparent viscosity of the brine / TEA / HEC mixture was measured at six different shear rates: 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm. Additionally, the initial pH of the brine / TEA / HEC mixture was measured. The brine / TEA / HEC mixture was then placed in an oven at 245 °F. After 20 hours, the brine / TEA / HEC mixture was removed from

the oven and allowed to cool to room temperature. After reaching room temperature, the apparent viscosity and pH of the mixture was again measured. After taking the measurement, the mixture was returned to the oven and left in the oven for 24 hours at 245 °F. Measurements of the pH and apparent viscosity were again taken after the mixture was allowed to cool to room temperature. The mixture was then returned to the oven for an additional 25 hours at 245 °F, after which the sample was allowed to cool and final measurements were taken.

[0021]   The results are summarized below:

Shear Rate (RPM)	Initial	20 Hrs	44 Hrs	75 Hrs
600	631 (estimated)	647 (estimated)	648 (estimated)	645 (estimated)
300	530	542	526	508
200	502	490	488	470
100	436	422	422	470
6	236	214	202	174
3	196	172	160	134
pH	7.57	7.3	7.44	7.33

TABLE 1: 13.3 ML TEA PRESENT (APPARENT VISCOSITY)

[0022]   Table 1 shows that the apparent viscosity of the brine / TEA / HEC mixture remained roughly constant during the entire 75 hour heat treatment. Further, the pH of the mixture also remained roughly constant. Based on these results, it is evident that the HEC polymer suffered no significant degradation during the entire 75 hour experiment when treated with TEA.

[0023]   For comparison, an experiment was run under conditions similar to those described above without the addition of TEA. In this experiment, 12.0 mL of an

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HEC suspension (41% by weight active component of HEC in dipropylene glycol methyl ether) was poured slowly into an agitated brine solution. As in the previous experiment, the brine solution consisted of 0.965 Lbbl of a 13.7 ppg $CaBr_2$ in water.

[0024]   Again, the initial apparent viscosity of the brine / HEC mixture was measured at six different shear rates: 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm. In addition, the initial pH was measured. As above, the brine / HEC mixture was placed in an oven at 245°F and measurements were taken after 20, 44, and 75 hours.

[0025]   The results are summarized below:

Shear Rate (RPM)	Initial	20 Hrs	44 Hrs	75 Hrs
600	596	662 (estimated)	420	166
300	504	506	294	93
200	460	452	238	65
100	396	372	154	35
6	204	142	16	4
3	164	102	10	3
pH	5.9	6	4.68	5.43

TABLE 2: COMPARATIVE RUN, TEA ABSENT (APPARENT VISCOSITY)

[0026]   As shown in Table 2, absent the TEA, viscosity reduction becomes significant at the times / temperatures associated with this experiment. For example, a dramatic loss in viscosity occurred within 44 hours into the experiment. Also noticeable is the fact that the pH of the system was significantly lower than that of the TEA-containing system described above. Thus,

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experimental evidence has determined that the TEA may provide a buffering effect to maintain the pH of the system at a pH of approximately 7. A discussion of why the buffering effect is believed to be significant is provided below.

[0027]   In a second embodiment, 49.4 mL of an HEC / TEA slurry was added to 0.859 Lbbl of a 14.18 ppg gallon $CaBr_2$ in water. The HEC/TEA slurry was formed by the addition of 91 pounds of TEA to 9 pounds of HEC powder. The resulting slurry, therefore, comprises 9% by weight HEC.

[0028]   As in the embodiment described with respect to Table 1, the initial apparent viscosity of the HEC slurry was measured at six different shear rates: 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm. In addition, the pH was measured. As above, the brine / HEC / TEA mixture was placed in an oven at 245°F and measurements were taken after 20, 47.5, and 73.5 hours, having allowed the solution to cool to room temperature before measuring.

[0029]   The results are summarized below.

Shear Rate (RPM)	Initial	20 Hrs	47.5 Hrs	73.5 Hrs
600	644 (estimated)	604 (estimated)	682 (estimated)	659 (estimated)
300	560	512	578	520
200	520	464	522	464
100	464	404	440	384
6	270	210	228	160
3	232	174	186	120
pH	7.44	7.35	7	7.2

TABLE 3: RESULTS FROM HEC/TEA SLURRY (APPARENT VISCOSITY)

[0030]   As in the first embodiment, it is apparent from examining the results in Table 3 that no significant viscosity degradation occurred. Polymer degradation causes a loss in viscosity because, as the polymer decomposes (a mechanism for this decomposition is proposed below), the high molecular weight chains become substantially lower molecular weight chains. As more low-molecular-weight chains are formed from the decomposition of the high molecular weight chains, the entanglements among the polymer chains decreases, which allows the polymer chains to flow more freely past one another and thereby decreases fluid viscosity. It is clear from Table 3 that even if the TEA is added as part of a polymer slurry, there is no reduction in the ability of TEA to increase the temperature stability of a polymer solution.

[0031]   In a third embodiment, the effects of TEA in the presence of other common additives was measured. Also, a suspension of HEC in synthetic oil rather than an organic solution was used to determine whether TEA would have a similar effect as in the other embodiments. Specifically, 12.5 mL of a suspension of HEC (41% active component HEC by weight in a synthetic oil solvent) was mixed into 0.916 Lbbl of a 13.9 ppg brine solution. In addition, a trace amount of an oxygen scavenger (sodium thiosulfate pentahydrate in this embodiment) was mixed as a dry reagent into the system. 13.3 mL of TEA was then added to the HEC / brine system. In this embodiment, $CaBr_2$ was used to create the brine solution.

[0032]   As in the above embodiment, the initial apparent viscosity of the brine / HEC mixture was measured at six different shear rates: 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm. In addition, the pH was measured. The brine / HEC / TEA mixture was placed in an oven at 245°F and measurements were taken after 21.5, 47, and 87 hours, allowing the mixture to cool to room temperature prior to measuring pH and viscosity.

[0033]   The results are tabulated below.

Shear Rate (RPM)	Initial	21.5 Hrs	47 Hrs	87 Hrs
600	510	731 (estimated)	623 (estimated)	670 (estimated)
300	410	625 (estimated)	510	520
200	400	570	400	468
100	306	490	400	396
6	154	264	192	160
3	130	220	152	118
pH	6.99	6.87	6.5	6.5

TABLE 4: HEC IN SYNTHETIC OIL SUSPENSION / OXYGEN SCAVENGER PRESENT (APPARENT VISCOSITY)

[0034]   It is apparent from Table 4 that changing the composition of the HEC suspension in the manner described above has no apparent effect on the ability of TEA to provide thermal stability to HEC polymers. In addition, it may be noted that, in this embodiment, the mixture was subjected to heat treatment for 87 hours. Even at this prolonged exposure, no major decomposition was noted. It may be noted that the presence of the oxygen scavenger appeared to have no effect on the mixture. Further, the pH of the system remained substantially constant, which is an indication that the TEA provides the same buffering effect as with higher HEC concentrations.

[0035]   As a comparison, 12.5 mL of a suspension of HEC (41% active component in a synthetic oil solution) was added to 0.916 Lbbl of a 13.9 ppg brine solution. To the HEC / brine mixture, 13.3 mL of TEA was added. As in the above embodiment, the brine solution comprised $CaBr_2$ in water.

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[0036]   As in the above embodiment, the initial apparent viscosity of the mixture was measured at six different shear rates: 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm. In addition, the initial pH was measured. As above, the brine / HEC / TEA mixture was placed in an oven at 245°F and measurements were taken after 21, 45, and 70 hours, allowing the mixture to cool prior to measuring.

[0037]   The results are tabulated below.

Shear Rate (RPM)	Initial	21 Hrs	45 Hrs	70 Hrs
600	280	633 (estimated)	624 (estimated)	578
300	214	526	494	510
200	186	496	494	420
100	146	426	368	344
6	56	224	156	132
3	44	182	118	96
pH	7.4	7.3	7	7

TABLE 5: HEC IN SYNTHETIC SUSPENSION/ NO OXYGEN SCAVENGER PRESENT

(APPARENT VISCOSITY)

[0038]   The above results confirm that the addition of an oxygen scavenger to the TEA / HEC / brine mixture has no significant effect on the ability of TEA to provide thermal stability to the polymer system.

[0039]   In a fourth embodiment, the effect of TEA on polymer stability in mixed brine systems was measured. In addition, the effect of TEA in the presence of lower concentrations of HEC suspensions was measured. Specifically, 43.8 pounds of a suspension of HEC (9% by weight of HEC suspended in ethylene glycol) was added to 0.796 Lbbl of 16.2 pounds per gallon $ZnBr_2$ / $CaBr_2$ in water.

The 16.2 pounds per gallon brine solution was formed by the dilution of a 19.2 pounds per gallon $ZnBr_2$ / $CaBr_2$ mixture with water. In this embodiment, the initial 19.2 pounds per gallon $ZnBr_2$ / $CaBr_2$ water mixture is 52.8% by weight $ZnBr_2$, 22.8% $CaBr_2$, with the balance water. To this, 19.9 pounds of TEA was added.

[0040]   As in the above embodiments, the initial apparent viscosity of the mixture was measured at six different shear rates: 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm. In addition, the pH was measured. The brine / HEC / TEA mixture was placed in an oven at 235°F and measurements were taken after 14, 35, and 52 hours, allowing the mixture to cool prior to measuring.

[0041]   The results are tabulated below.

Shear Rate (RPM)	Initial	14 Hrs	35 Hrs	52 Hrs
600	660 (estimated)	354	124	72
300	582	226	64	37
200	526	168	44	25
100	456	96	22	12
6	266	6	2	1
3	226	4	1	0
pH	3.8	4	4.1	4.3

TABLE 6: MIXED BRINE SOLUTION (APPARENT VISCOSITY)

[0042]   As shown in Table 6, viscosity reduction becomes significant at the times / temperatures associated with this experiment, despite the presence of TEA. For example, a dramatic loss in viscosity has occurred 14 hours into the experiment. Also noticeable is that the pH of the system was significantly lower than that of

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the TEA containing systems described above. The loss of viscosity even in the presence of TEA was attributed to the low pH of this system. The propensity of zinc bromide brines to cause low pH has previously been noted, for example, in U.S. Patent No. 6,100,222, issued to Vollmer, *et al.* Basically, the inherent acidity of zinc bromide brines leads to the relatively low pH's measured in Table 6.

[0043]   For comparison, an experiment was run under similar conditions as above, but the relative concentration of $ZnBr_2$ was decreased. Specifically, 36.2 pounds of a suspension of HEC (9% by weight of HEC suspended in ethylene glycol) was added to 0.855 Lbbl of 16.2 pounds per gallon $ZnBr_2$ / $CaBr_2$ in water. The 16.2 pounds per gallon brine solution was formed by the dilution of a 19.2 pounds per gallon $ZnBr_2$ / $CaBr_2$ mixture (having the same composition as in the above embodiment) with 14.2 pounds per gallon $CaBr_2$ in water. To this, 12.8 pounds of TEA was added.

[0044]   As in the above embodiments, the initial apparent viscosity of the mixture was measured at six different shear rates: 600 rpm, 300 rpm, 200 rpm, 100 rpm, 6 rpm, and 3 rpm. In addition, the pH was measured. The brine / HEC / TEA mixture was placed in an oven at 250°F and measurements were taken after 22.5, 39, 61, 78.5, and 93.5 hours, allowing the mixture to cool prior to measuring.

[0045]   The results are tabulated below.

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Shear Rate (RPM)	Initial	22.5 Hrs	39 Hrs	61 Hrs	78 Hrs	93.5 Hrs
600	568 (estimated)	606 (estimated)	576	588	574	534
300	502	494	450	460	432	400
200	444	436	394	398	370	338
100	372	358	314	308	280	248
6	208	160	108	98	66	50
3	178	124	76	58	40	28
pH	5.2	5.3	5.9	5.8	5.9	5.8

TABLE 7: LOWER RELATIVE ZINC (APPARENT VISCOSITY)

[0046]   As shown in Table 7, viscosity reduction becomes significant at the times / temperatures associated with this experiment, despite the presence of TEA. However, the viscosity reduction is not as great as the reduction seen in Table 6. It also may be noted that the pH's in Table 7 are higher (less acidic) than those seen in Table 6. This experimental evidence further supports the mechanism described below.

[0047]   Like HEC, TEA is miscible in water, which prevents any undesirable phase separation. While the foregoing embodiments reference a limited number of compounds, it should be recognized that chemical compounds having the same general characteristics also will function in an analogous fashion. For example, it is expressly within the scope of the present invention that methyldiethanol amine (MDEA), dimethylethanol amine (DMEA), diethanol amine (DEA), monoethanol amine (MEA), or other suitable tertiary, secondary, and primary amines and ammonia could be substituted, in whole or in part, for the triethanol amine described herein. In addition, it also is expressly within the scope of the invention

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that other mixed TEA systems may be used as additives, such as a TEA / glycol system or a TEA / alcohol system. Suitable alcohols would include methanol, ethanol, n-propanol and its isomers, n-butanol and its isomers, n-pentanol and its isomers, n-hexanol and its isomers, *etc.*

[0048]   Similarly, other natural and natural derivative polymers may be substituted for HEC, such as, for example, starch, derivatized starch, or xanthan gum. Furthermore, it should be noted that while the above examples discuss the utility of amines in $CaCl_2$ containing brine solutions, it will be clear to one of ordinary skill in the art that other brine solutions, such as $ZnCl_2$, $CaBr_2$, and $ZnBr_2$, NaCl, KCl, NH_4Cl, $MgCl_2$, seawater, NaBr, $Na_2S_2O_3$, and combinations thereof, may be used.

[0049]   In addition, while specific amounts of the chemicals used are described in the above embodiments, it is specifically within the contemplation of the invention that amounts different than those described above may be used to provide the desired thermal stability, depending on the particular application. For example, in one embodiment, a suitable system for increasing polymer stability may comprise 0.1 % by weight to 50 % by weight HEC and 0.1% by weight to 50 % by weight TEA. More preferably, in one embodiment the system may comprise 0.1 % by weight to 5% by weight HEC and 0.2% by weight to 20% TEA. Still more preferably, in one embodiment the system may comprise 0.3% by weight to 1.5% by weight HEC and 0.5% by weight to 10% by weight TEA.

[0050]   Therefore, in some embodiments, it is expressly within the scope of the invention that no water or brine will be present. In addition, no limitation should be placed on the use of other systems such as a TEA / glycol / HEC system or a TEA / glycol / HEC / brine system. Other systems expressly within the scope of the present invention include TEA / alcohol additives.

[0051]   One proposed mechanism for how the addition of TEA provides additional thermal stability is based on the belief that TEA may act as a pH buffer. Because HEC is derived from cellulose, many of the reactions that are associated with cellulose are relevant to the chemistry of HEC and other related biopolymers (such as starch). Specifically, acid catalyzed hydrolysis can cause degradation of cellulose. Acids (which are present in downhole formations because of the release of acid gases such as H_2S) attack the acetal linkages, cleaving the 1-2 glycosidic bond, as labeled in Equation 1. The carbon atom labeled 2 in Equation 1 may be considered an acetal. Generally speaking, an acetal is simply a diether in which both ether oxygens are bound to the same carbon. Acetals typically are much more stable toward alkali and, base-catalyzed hydrolysis is much less likely to occur. Thus, by keeping the pH above the base brine pH, or as near to 7 as possible, TEA may serve to prevent an acid-catalyzed degradation of HEC.

[0052]   In the above discussion involving an acid-catalyzed mechanisms for polymer degradation, it should be noted explicitly that both Bronsted-Lowry and Lewis definitions of acids are equally applicable. Thus in aqueous systems where acids may be present and acting as such through the Bronsted-Lowry definition of an acid, the role of the acid would be that of a "proton-donor" while the complementary role of the TEA would be that of a "proton-acceptor". Furthermore, in systems such as, for example, those containing the Lewis acid zinc bromide, where the acid may be acting as such through the Lewis definition of an acid, the role of the acid would be that of an "electron-acceptor" while the complementary role of the TEA would be that of a "electron-donor."

[0053]   Another embodiment of this invention is the ability of the TEA to improve the hydration time of HEC and the transition temperature at which solutions of HEC in monovalent brines (such as KCl and NaCl) 'salt out,' or separate into distinct phases (i.e., syneresis). Typically this phase separation manifests by the appearance of a phase of higher than original HEC concentration, usually floating

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on top of a lower viscosity layer. In many cases, the HEC will actually precipitate completely out of solution.

[0054]   Two 10.0 lbm/gal NaCl brines, one treated with 0.043 vol% TEA and the other untreated, were used to measure the effect of TEA on hydration time and transition temperature. Both brines were viscosified with Union Carbide HEC 10 at 4 lbm/bbl concentration. Both samples viscosified, however, the TEA treated brine developed full viscosity in several minutes whereas the untreated brine required over 1 hour of mixing to fully viscosify. Thus, the addition of TEA significantly improved the hydration time.

[0055]   Initial rheology measurements of the two fully viscosified brines were taken using a Fann 35 rheometer at room temperature. The solutions were then heat-aged in an oven at 180 °F for 22 hours, and then removed and allowed to cool to room temperature. Rheological measurements on both brines were then taken on the Fann 35. As can be seen in Table 8 below, the TEA-treated solution was homogeneous in appearance and rheological properties, whereas the untreated solution formed separate phases in which HEC was concentrating and salting out of solution, with the top phase considerably more viscous than the lower phase, but neither phase quite so viscous as the homogeneous TEA-treated solution. Clearly, some of the HEC salted-out and no longer contributed fully to the viscosity of the un-TEA-treated fluid.

[0056]   The results are tabulated below.

Dial Reading (rpm)	Initial		After Heat Aging			
	Untreated	TEA-Treated	Untreated Bottom Layer	Untreated Top Layer	TEA-Treated Bottom Portion	TEA-Treated Top Portion
600	321 (est.)	285	100	230	258	255
300	260	235	77	190	215	210
200	236	213	65	168	192	187
100	200	179	49	137	157	152
6	90	77	12	51	52	50
3	73	59	8	37	35	33

TABLE 8: EFFECT OF TEA ON HYDRATION TIME AND TRANSITION TEMPERATURE

[0057]   Table 8 shows that, after heat aging, there is substantially no difference in viscosity between the top and bottom portion of the HEC / brine / TEA solution. However, after heat aging, Table 8 shows that distinct phases exist in the HEC / brine solution. Specifically, the bottom layer in the non-TEA containing solution, has a substantially loss in viscosity, which may be attributed to the aforementioned 'salt out' effect.

[0058]   The present invention advantageously increases the effective temperature range for natural polymer systems in an inexpensive, easy-to-implement method. The addition of miscible amines into the polymer system dramatically increases the temperature resistivity of the solution. Further, the present invention advantageously improves the hydration time and the transition temperature of natural polymer systems in monovalent brines.

[0059]   While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the

scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.